

# A Prebiotic Surface Catalyzed Photochemically Activated Synthesis of Vitamin B12

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**Abstract:** - The four stereospecific pyrroline derivatives present in the corrin structure of Vitamin B12 may be oligomerized to form a corrin structure or a porphin structure. The analogous porphin structure is formed with a lower activation energy and favourable free energy change. The corresponding corrin structure requires a greater activation energy and gives a less favourable free energy change. The resulting corrin structure may then chelate a metal ion and accept a propyne adduct in a stereospecific manner which subsequently binds metaphosphoric acid. The charge transfer adduct is cleaved by the partially hydrolyzed cyanopropyne substituent of ring D. The corrin structure is then free to bind five carbon monoxide molecules to form aziridin-2-one adducts. These can be photochemically activated to form the  $\alpha$ -D-ribose and add a hydrogen ion. A carbonyl reaction site is then available to bond with the rare 5,6-dimethyl benzimidazole base. Further hydrogenation frees the sugar and rotation allows the bonding of the rare base to the metal ion. The reactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2 /6-31G\* level.

**Key-Words:** Pyrroline monomers, corrin, porphin,  $\alpha$ -D-ribose, 5,6-dimethyl benzimidazole, Vitamin B12.

## 1 Introduction

Vitamin B12, cobalamin [1], is a highly conjugated cyclic chromophoric molecule containing the corrin structure [2] chelating a cobalt ion which may be present in oxidation states 1,2 or 3. The cobalt ion may also accept coordination from deoxyadenosyl, cyanide, hydroxide ions, water and 5,6-dimethylbenzimidazole [3,4]. It is an essential vitamin to prevent pernicious anaemia [5] where it acts as a cofactor to form holoenzymes from the adenosylcobalamin dependent isomerases, the methyl cobalamin dependent methyl transferases and dehalogenases [3]. In the action of the isomerases a hydrogen atom is transferred from the substrate to an adjacent atom site. In the methyl transfer reactions a methyl group coordinated to the cobalt ion is transferred to an acceptor. In anaerobic dehalogenation it facilitates reductive dehalogenation in which a bound chlorine atom forms hydrogen chloride.

The biosynthesis of the active vitamin has been achieved from the amino laevulinic acid [5]. Neither animals or plants can manufacture B12, just microorganisms [5].

From a prebiotic perspective [6] it is desirable if the reactant molecules formed spontaneously from a

supposed prebiotic atmosphere to be inevitably present. It has often been held that the atmosphere of the Earth was originally mildly reducing [5,7] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is also supposed that alkynes such as acetylene [8,9] were present as found on Titan, a moon of Saturn. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [10] and polyenes [11].

This paper proposes a model for the surface catalytic photochemically activated formation of the corrin structure from the gases, propyne, ethyne, hydrogen cyanide and hydrogen with the surface catalyst, magnesium porphin. Experimental gaseous mixtures subjected to discharge have been shown to produce biomolecules [12].

## 2 Problem Formulation

The computations tabulated in this paper used the GAUSSIAN98 [13] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections (HF) [14], together with scaling [15], using the same basis set, 6-31G\*, are as previously published [6]. All zero

point energies are calculated at the HF level of accuracy. Enthalpy changes calculated at the MP2 level with scaled HF zero point energies are designated,  $\Delta H$ , those calculated at the HF level with scaled HF zero point energies are designated  $\Delta H_{(HF)}$ . The charge transfer complexes are less stable when calculated at the Hartree Fock level [14].

If the combined energy of the products is less than the combined energy of the reactants it may show that the reaction is also likely to be spontaneous at higher temperatures. This paper uses the atomic unit of energy, the hartree [13].

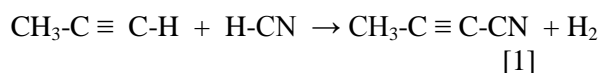
$$1h = 627.5095 \text{ kcal.mol}^{-1}$$

$$1h = 4.3597482 \times 10^{-18} \text{ J}$$

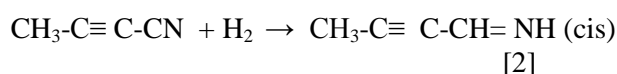
### 3 Problem Solution

#### 3.1 Total energies (hartrees)

Molecules that are present interstitially and in planets [16,17] are here taken to be the initial reactant molecules: propyne, ethyne and hydrogen cyanide, where the formation of the but-2-yne nitrile and but-2-ynimine (cis) may be produced by atmospheric free radical or ionic reactions [17].

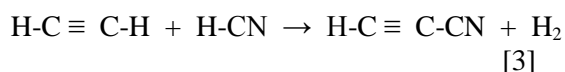


$$\Delta H = -0.00816 \text{ h}$$

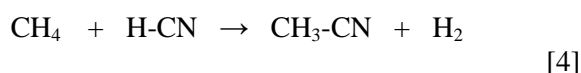


$$\Delta H = 0.00444 \text{ h}$$

Further reactants are taken to be cyanoacetylene [16] and methyl cyanide [17], also formed atmospherically by the reactions,

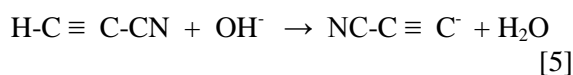


$$\Delta H = -0.00382 \text{ h}$$

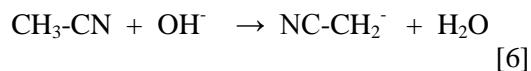


$$\Delta H = 0.00307 \text{ h}$$

It is also assumed that the environment was mildly alkaline due to the presence of ammonia in the reducing atmosphere, so that the anions may be formed according to the equations,



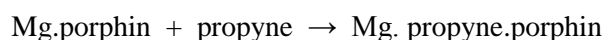
$$\Delta H = -0.09794 \text{ h}$$



$$\Delta H = -0.04799 \text{ h}$$

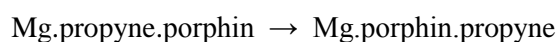
Mg.porphin is a powerful catalyst able to form charge transfer complexes with a number of different kinds of molecules [18].

With the adduct of propyne with Mg.porphin, the propyne is positively charged +0.073 [11].



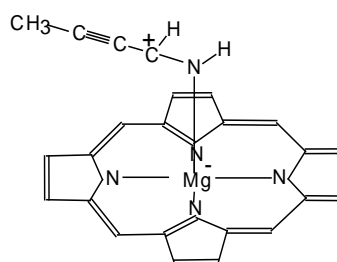
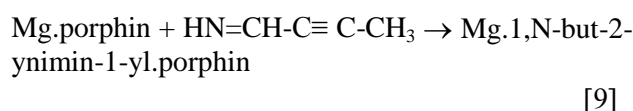
$$\Delta H = -0.00209 \text{ h} \quad [7]$$

However, it is also possible for the propyne to migrate to bond with a pyrrole nitrogen atom to form a high energy complex [11].



$$\Delta H = 0.01862 \text{ h} \quad [8]$$

The catalyst also forms a weak charge transfer complex with but-2-ynimine where the ligand is positively charged (0.07) and the porphin has a negative charge, as shown,



Mg.1,N-but-2-ynimin-1-yl.porphin (cis) (1)

$$\Delta H = -0.04014 \text{ h}$$

Mg.porphin may also form an adduct with acetylene [19],

$$\Delta H = -0.01807 \text{ h}$$

The data for the total energies and zero point energies for the HF and MP2/6-31G\* equilibrium geometries for these molecules and others involved in the synthesis are given in Table.1.

Table 1  
MP2 /6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
Mg,1,N-but-2-ynimin-1-yl.porphin (cis) (1)	-1394.57494	0.37950
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl $\Delta^1$ - pyrroline <sup>+1</sup> C <sub>11</sub> H <sub>12</sub> N <sub>3</sub> <sup>+</sup>		
Monomer A (2)	-585.94178	0.173521
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl $\Delta^1$ - pyrroline <sup>+1</sup> C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> <sup>+</sup>		
Monomer B (3)	-625.12035	0.20245
3-cyanoethynyl-4-4'-dimethyl-5-methenyl $\Delta^1$ - pyrroline <sup>+1</sup> (4) C <sub>10</sub> H <sub>9</sub> N <sub>2</sub> <sup>+</sup>		
Monomer C (4)	-493.95240	0.17420
3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl $\Delta^1$ - pyrroline <sup>+1</sup> C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> <sup>+</sup>		
Monomer D (5)	-625.12956	0.20389
but-2-yne nitrile	-208.25777	0.05963
but-2-ynimine	-209.41044	0.08479
Mg.porphin	-1185.12250	0.29262
Mg.OH.porphin <sup>-1</sup>	-1260.79369	0.29802
propyne	-116.24181	0.06010
ethyne	-77.06679	0.02945
H-C $\equiv$ C-CN	-169.07910	0.02976
NC-C $\equiv$ C <sup>-</sup>	-168.49375	0.01711
CH <sub>3</sub> -CN	-132.33825	0.04840
NC-CH <sub>2</sub> <sup>-</sup>	-131.70120	0.03278
H-CN	-93.15894	0.01593
CH <sub>4</sub>	-40.33255	0.04778
H <sub>2</sub>	-1.14414	0.01059
OH <sup>-</sup>	-75.51314	0.00885
H <sub>2</sub> O	-76.19685	0.02298

### 3.2 The overall stoichiometry for the formation of the four monomers that oligomerize to corrin derivatives.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry for the synthesis of corrin derivatives from but-2-ynimine, propyne, ethyne, methyl cyanide and cyanoacetylene can be represented as follows, where the final hydrogenation and hydrolysis present in the vitamin B12 structure is yet to occur. Here the reactions given are those that lead to the stereospecificity depicted in Fig.1 for a corrin derivative with similar stereochemistry to that found in Vitamin B12 [2].

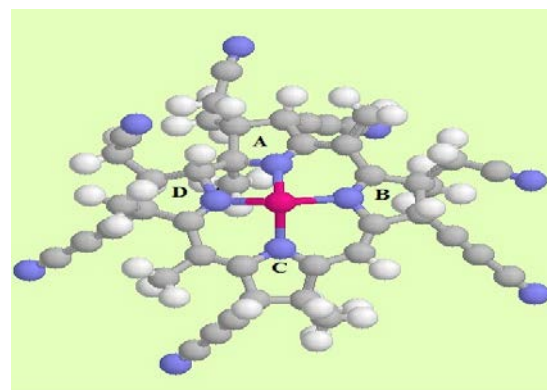
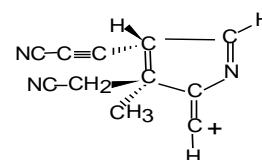
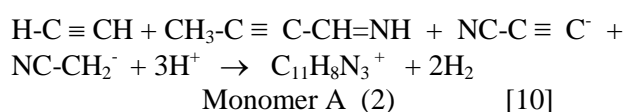


Fig.1. The designation of the corrin rings as recommended by IUPAC [2].

The monomer that forms ring A [2] is formed as follows:



3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl  $\Delta^1$ - pyrroline<sup>+1</sup> Monomer A (2)

$$\Delta H = -1.53068 \text{ h}$$

The monomer that forms ring B [2] is formed as follows:

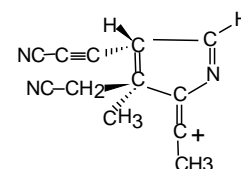
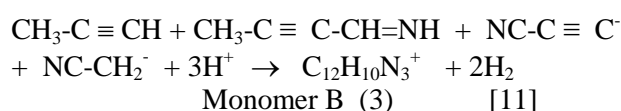
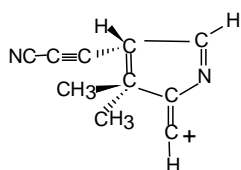
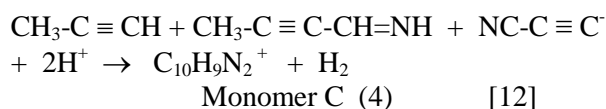


Fig.2. 3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl  $\Delta^1$ - pyrroline<sup>+1</sup> (3)

$$\Delta H = -1.54041 \text{ h}$$

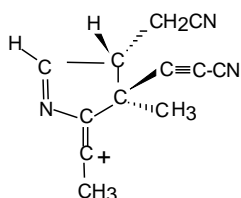
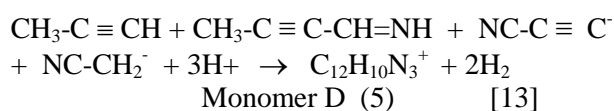
The monomer that forms ring C [2] is formed as follows:



3-cyanoethynyl-4-4'-dimethyl-5-methenyl  $\Delta^1$ -pyrroline<sup>+1</sup> (4)

$$\Delta H = -0.93026 \text{ h}$$

The monomer that forms ring D [2] is formed as follows:



3-cyanomethanyl-4-cyanoethynyl-4-methyl-5-ethenyl  $\Delta^1$ -pyrroline<sup>+1</sup> (5)

$$\Delta H = -1.54369 \text{ h}$$

The enthalpy changes are negative indicating that there may be energetically favourable routes to the formation of each of these monomers from these reactants [20-21].

### 3.3 The Formation of dimers of monomers A, B, C and D

#### 3.3.1. The formation of the dimer from monomers A and B.

The monomers A and B are highly reactive, readily undergoing ring expansion, exocyclic ring formation, inter-pyrroline bonding and protonic shift. This limits the accuracy of characterizing these molecules.

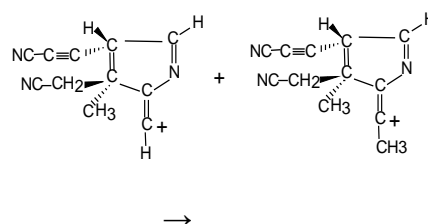
The data for the total energies and zero point energies for the HF and MP2/6-31G\* equilibrium geometries for these molecules and others involved in the synthesis are given in Table.2.

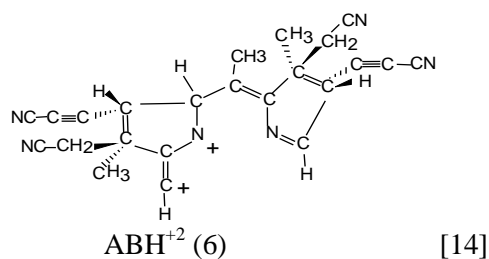
Table 2

MP2 /6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
1-(3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanoethynyl-4-cyanomethanyl-4-methyl- $\Delta^1$ -pyrrolin-5yl) -1-methyl methene <sup>+</sup> . Dimer ABH <sup>+2</sup> (6)	-1211.02018	0.37631
1-(3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanoethynyl-4-cyanomethanyl-4-methyl- $\Delta^1$ -pyrrolin-5yl) -1-methyl methene <sup>+</sup> . Dimer AB <sup>+1</sup> (7)	-1210.89564	0.36531
1-(3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanoethynyl-4,4'-dimethyl- $\Delta^1$ -pyrrolin-5yl) -1-methene <sup>+2</sup> . Dimer BCH <sup>+2</sup> (8)	-1119.00987	0.37731
1-(3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanoethynyl-4,4'-dimethyl- $\Delta^1$ -pyrrolin-5yl) -1-methene <sup>+1</sup> . Dimer BC <sup>+1</sup> (9)	-1118.90632	0.37326
1-(3-cyanoethynyl-4-4'-dimethyl-5-methenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanomethanyl-4-cyanoethynyl-4-methyl- $\Delta^1$ -pyrrolin-5yl) -1-methyl methene <sup>+</sup> . Dimer CDH <sup>+2</sup> (10)	-1119.00546	0.37646
1-(3-cyanoethynyl-4-4'-dimethyl-5-methenyl $\Delta^1$ -pyrrolin-2yl)-1'-(3-cyanomethanyl-4-cyanoethynyl-4-methyl- $\Delta^1$ -pyrrolin-5yl) -1-methyl methene <sup>+</sup> . Dimer CD <sup>+1</sup> (11)	-1118.87726	0.37113

They may easily engage in dimerization with an activation energy of 0.157 h, as shown,

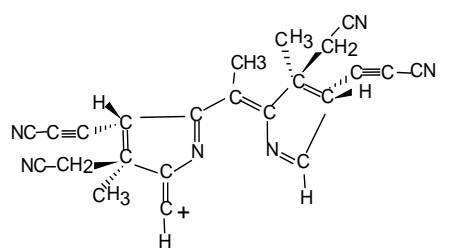




[14]

$$\Delta H = 0.04225 \text{ h}$$

with the subsequent elimination of a proton in the mildly alkaline medium to form a corrin derivative further stabilized by ions such as Mg<sup>++</sup>.



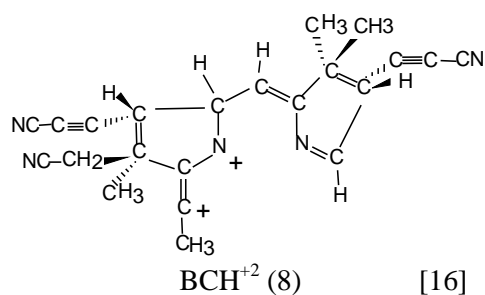
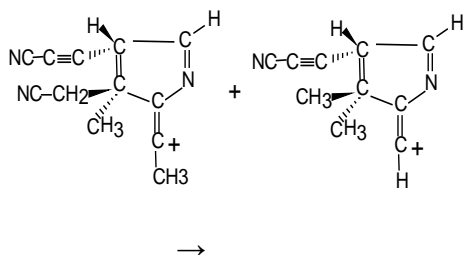
[15]

1-(3-cyanoethyl-4-cyanomethyl-4-methyl-5-methenyl  $\Delta$ 1- pyrroline-2yl)-1'-(3-cyanoethyl-4-cyanomethyl-4-methyl-  $\Delta$ 1- pyrrolin-5yl) -1-methyl methene<sup>+</sup>

$$\Delta H = -0.55639 \text{ h}$$

### 3.3.2. The formation of the dimer from monomers B and C.

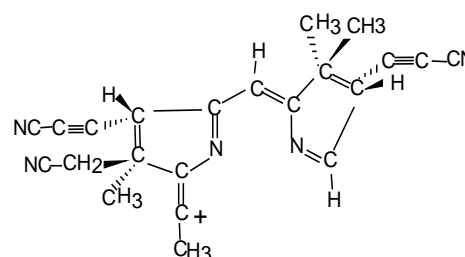
The monomers B and C are highly reactive and may easily engage in dimerization with an activation energy of 0.219 h, as shown,



[16]

$$\Delta H = 0.06346 \text{ h}$$

with the subsequent elimination of a proton in the mildly alkaline medium to form a corrin derivative further stabilized by ions such as Mg<sup>++</sup>.



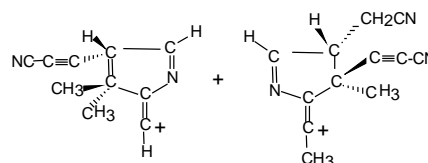
[17]

1-(3-cyanoethyl-4-cyanomethyl-4-methyl-5-ethenyl  $\Delta$ 1- pyrrolin-2yl)-1'-(3-cyanoethyl-4,4'-dimethyl-  $\Delta$ 1- pyrrolin-5yl) -1- methene<sup>+</sup>

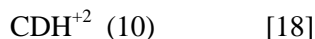
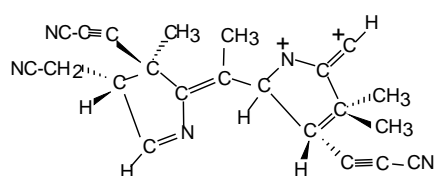
$$\Delta H = -0.57119 \text{ h}$$

### 3.3.3. The formation of the dimer from monomers C and D.

The synthesis of Monomers C and D as depicted here is predicated on the formation of weak complexes calculated as charge transfer and van der Waals, which may be orientated to form stereospecific di-adducts by the magnetic field of exciting radiation. The monomers C and D are highly reactive and may easily engage in dimerization with an activation energy of 0.133 h, as shown,

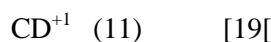
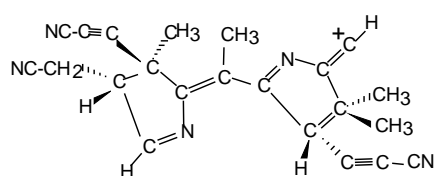


→



$$\Delta H = 0.07504 \text{ h}$$

and the formation of a dimer in the mildly alkaline solution, as shown,



1-(3-cyanoethynyl-4'-dimethyl-5-methenyl  $\Delta$ 1-pyrroline-2yl)-1'-(3-cyanomethanyl-4-cyanoethynyl-4-methyl-  $\Delta$ 1-pyrroline-5yl) -1-methyl methene<sup>+</sup>

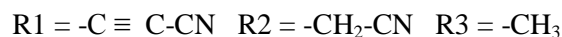
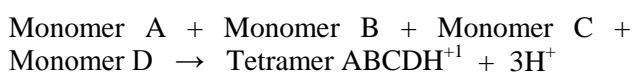
$$\Delta H = -0.54767 \text{ h}$$

The dimer is further stabilized with ions such as  $\text{Mg}^{++}$ , as a prerequisite for the formation of corrin derivatives.

### 3.4 The Formation of trimmers and tetramers from monomers A, B, C and D

The four monomers may form trimers (64) and tetramers (256) by consecutively adding monomers followed by de-protonation before the next monomer addition, or by forming the oligomer and final complete de-protonation. Alternatively, the dimers and trimmers, deprotonated or not, may react to give the oligomers.

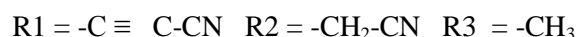
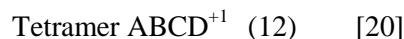
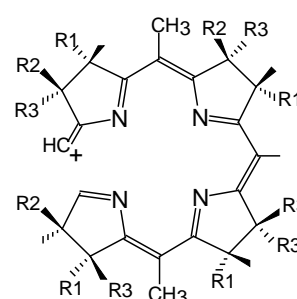
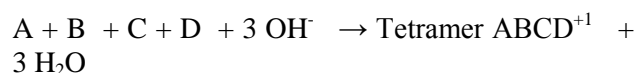
Here the formation of one open chain tetramer is depicted as corresponding to the structure found in Vitamin B12 [2]. The rotamers of the side chains are directed away from the centre of the molecule. They have a very minor effect on the energy of the molecule. The designation of these molecules is a non-standard abbreviation.



$$\Delta H = 0.49882 \text{ h}$$

It is assumed that the above activation energies (0.21 h) as supplied by photochemical excitation are sufficient for the formation of the tetramer.

The tetramer may react with the mildly alkaline medium to give an open chain tetramer, as shown,



$$\Delta H = -1.51589 \text{ h}$$

The overall enthalpy change is favourable for the formation of the tetramer.

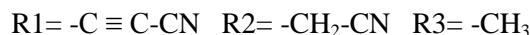
As the iteration time becomes prohibitive for molecules in excess of 100 atoms [14] the model has had to be reduced to HF for these calculations, and there is also an excessive demand on hardware resources and modeling programs.

The data for the total energies and zero point energies for the HF equilibrium geometries for these molecules and others involved in the synthesis are given in Table.3.

Table 3  
MP2 /6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	HF hartree	ZPE (HF) hartree
Tetramer ABCD <sup>+1</sup> (12)	-2322.21779	0.73373
CORRIN <sup>+1</sup> (13)	-2321.97484	0.73677
CORRIN <sup>+1</sup> (14)	-2323.25070	0.76621

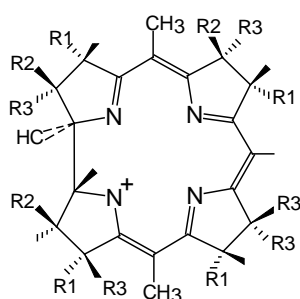
PORPHIN <sup>+1</sup> (15)	-2322.12746	0.73320
PORPHIN (16)	-2321.83429	0.72920



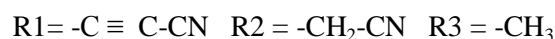
$$\Delta H = -0.13225 \text{ h}$$

### 3.5 The formation of the cyclic corrin and the analogous porphin tetramers from monomers A, B, C and D

The formation of the corrin contracted structure is here assumed to occur with the formation of the C-C bridging bond and a methine group with the same order of activation energy as shown above for the formation of dimers, trimers and tetramers,



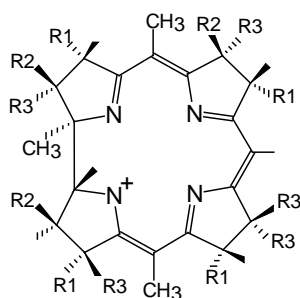
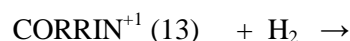
CORRIN<sup>+1</sup> (13) [21]



$$\Delta H = 0.24566 \text{ h}$$

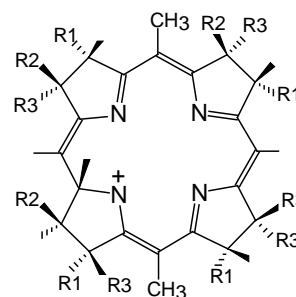
The activation energy to close the ring was calculated as 0.269 h, and 0.026 for the reverse reaction.

The hydrogenation of the methine group is a favourable reaction which fixes the structure and limits the conjugation, as shown,



CORRIN<sup>+1</sup> (14) [22]

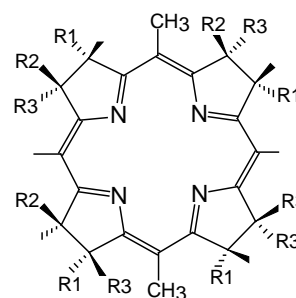
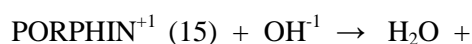
The formation of the analogous porphin structure also requires an activation energy, calculated as 0.078 h to close the ring and 0.001 to open it.



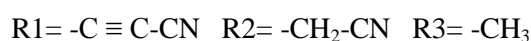
PORPHIN<sup>+1</sup> (15) [23]

$$\Delta H = 0.08987 \text{ h}$$

However, it may become deprotonated in a favourable reaction to give a neutrally charged porphin structure,



PORPHIN (16) [24]



$$\Delta H = -0.38196 \text{ h}$$

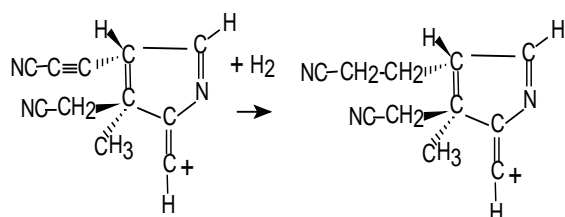
The sum of these reactions indicates that the porphin structure is formed with a lower enthalpy change a

and with a combined more favourable enthalpy change if the de-protonation is included, whereas this de-protonation cannot occur with the corrin structure and this is not comparably compensated by the hydrogenation.

### 3.6 The formation of the link from the cyclic corrin structure to the $\alpha$ -D-ribose of the Vitamin B12 structure.

#### 3.6.1. The transformation of the cyanoethynyl substituent on D-ring.

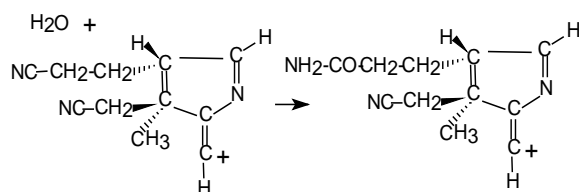
To form a link with the  $\alpha$ -D-ribose structure to be formed on its surface one of the cyanoethynyl substituents, the one bonded to carbon atom 3, [2] of the D-ring of the substituted corrin was hydrogenated and hydrolysed to the amide structure as found in Vitamin B12, according to the following equations.



3-cyanoethanyl-4-cyanomethanyl-4-methyl-5-methenyl  $\Delta$ 1- pyrroline (17) [25]

$$\Delta H_{(\text{HF})} = -0.12170 \text{ h}$$

The partial hydrolysis is as shown,



3-(2-carbamoyl ethanyl)-4-cyanomethanyl-4-methyl-5-methenyl  $\Delta$ 1- pyrroline (18) [26]

$$\Delta H_{(\text{HF})} = -0.04585 \text{ h}$$

The data for the total energies and zero point energies for the MP2 or HF equilibrium geometries for these molecules and others involved in the synthesis are given in Table.4.

Table 4

MP2 or HF /6-31G\* total energies and zero point energies (hartrees) for the respective equilibrium geometries

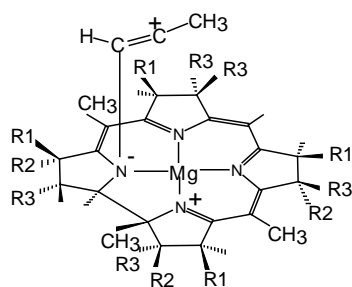
Molecule	HF / MP2 hartree	ZPE (HF) hartree
3-cyanoethanyl-4-cyanomethanyl-4-methyl-5-methenyl $\Delta$ 1- pyrroline (17)	-586.48178 / -588.35914	0.22277
3-(2-carbamoyl ethanyl)-4-cyanomethanyl-4-methyl-5-methenyl $\Delta$ 1- pyrroline (18)	-662.55064 / -664.61460	0.25952
Mg.corrin.propyne <sup>+3</sup> (19)	-2638.16157	0.83685
Mg.corrin.prop-1-ylum-2- metaphosphate <sup>+3</sup> (20)	-3204.12304	0.86518
Mg.3-(2-carbamoyl ethanyl) corrin. prop-1-ylum-2-.metaphosphate <sup>+3</sup> (21)	-3282.61544	0.94500
Mg.3-(2-ethanyl carboxamido)-corrin-N.prop-1-ylum-2-.metaphosphate <sup>+3</sup> (22)	-3282.57208	0.95396
Mg.3-(2-ethanyl carboxamido)-corrin-N.prop-1-ylum-2-.metaphosphate <sup>+3</sup> (22)	-3282.58724	0.94519
corrin <sup>+3</sup> (24)	-1268.82904 / -1265.32793	0.48685
Mg.corrin.5CO <sup>+3</sup> (25)	-1833.39709	0.53955
Mg.corrin.5CO.H <sup>+4</sup> (26)	-1833.73900	0.54448
Mg.corrin.4CO.C(OH)NH <sub>2</sub> .H <sup>+4</sup> (27)	-1890.12727	0.58428
Mg.corrin <sup>+3</sup> (28)	-2232.11112	0.69334
Mg.corrin <sup>+4</sup> (29)	-2854.15485	0.86946
Mg.corrin <sup>+3</sup> (30)	-2854.14056	0.88490
Mg.corrin <sup>+3</sup> (31)	-2857.82882	0.92456
Mg.corrin <sup>+3</sup> (32)	-2781.79249	0.90158
Mg.corrin <sup>+3</sup> (33)	-2781.88449	0.91015
HPO <sub>3</sub>	-565.92320 / 565.92320	0.02542
NH <sub>3</sub>	-56.35421 / 56.18436	0.03700
H <sub>2</sub> O	-76.19685 / -76.01075	0.02298
CO	-112.737 88 / -113.02122	0.00556
H <sub>2</sub>	-1.12683 / -1.14414	0.01059
H	-0.42244	

#### 3.6.2. The addition of propyne to bond with a pyrroline nitrogen on D-ring.

The gas propyne is able to bond to the magnesium ion of corrin or to form a higher energy state bonded to a pyrroline nitrogen atom [10 ], as shown,





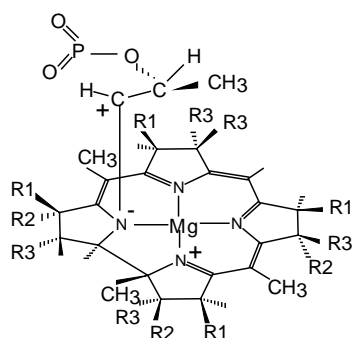
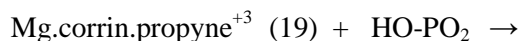
Mg.corrin.propyne<sup>+3</sup> (19) [27]

$$\Delta H_{(\text{HF})} = -0.01304 \text{ h}$$

With this charge transfer adduct the C2 of the propyne adduct carries a Mulliken charge [13] of 0.40.

### 3.6.3. The addition of metaphosphoric acid to the Mg.corrin.propyne<sup>+3</sup> adduct.

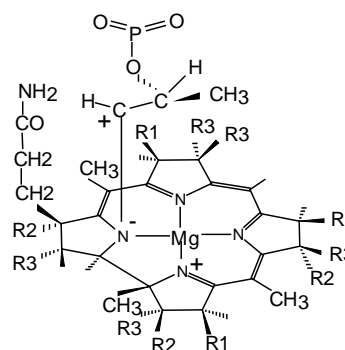
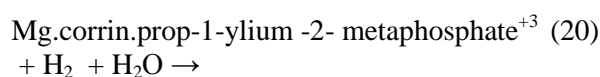
The formation of the phosphate linkage is here represented as the reaction with a monomeric form of metaphosphoric acid although the exact phosphorous acid and mechanism are not known,

Mg.corrin.prop-1-ylum-2- metaphosphate<sup>+3</sup> (20) [28]

$$\Delta H_{(\text{HF})} = -0.03146 \text{ h}$$

The activation energy was calculated as 0.038 h by stretching the O-C bond. Although both stereoisomers are of comparable energy it is expected that a steric advantage pertains to the isomer depicted as it is rotated anticlockwise against the methyl group on C19 of the corrin owing to the magnetic field of the radiation when viewed from above the ring [10].

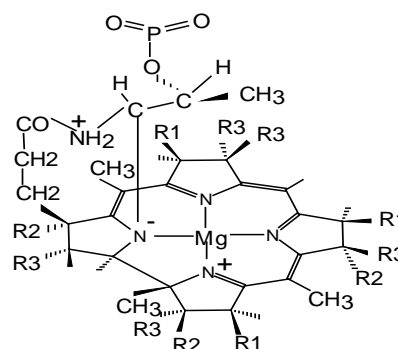
### 3.6.4. The hydrogenation and hydrolysis of the substituent on carbon 3 of the Mg.corrin.propyn.metaphosphate<sup>+1</sup> adduct.

Mg.3-(2-carbamoyl ethanyl) corrin. prop-1-ylum-2-.metaphosphate<sup>+3</sup> (21) [29]

$$\Delta H_{(\text{HF})} = -0.263729 \text{ h}$$

### 3.6.5. The bonding of the C3 amide to the N. prop-1-ylum metaphosphate of the adduct.

Mg.3-(2-carbamoyl ethanyl) corrin. prop-1-ylum-2-.metaphosphate<sup>+3</sup> (21)  $\rightarrow$

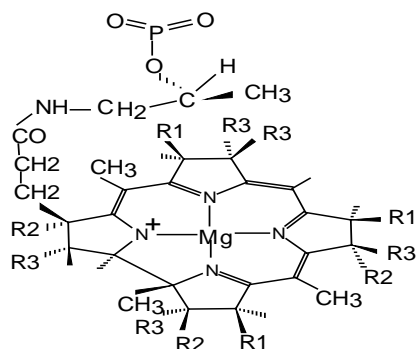
Mg.3-(2-ethanyl carboxamido)-corrin-N.prop-1-ylum-2-.metaphosphate<sup>+3</sup> (22) [30]

$$\Delta H_{(\text{HF})} = 0.05133 \text{ h}$$

### 3.6.6. The formation of 1-methyl 2-(3-Mg.corrinyl-2-ethanyl carboxamido) ethan-1-metaphosphate.

With an activation energy of 0.124 h the Mg.3-(2-ethanyl carboxamido)-corrin-N.prop-1-ylum-2-.metaphosphate<sup>+3</sup> (22) <sup>3</sup> adduct can transfer a proton and remain as an unreactive substituent of the corrin whilst the  $\alpha$ -D-ribose forms

on the corrin template. The reverse reaction was calculated as having an activation energy of 0.087 h.



Mg.3-(2-ethyl carboxamido)-corrin-N-prop-1-yl-ium-2-.metaphosphate<sup>+3</sup> (23) [31]

$$\Delta H_{(\text{HF})} = -0.03389 \text{ h}$$

### 3.7 The formation of $\alpha$ -D-ribose on the substituted corrin template

#### 3.7.1. The formation of a carbon monoxide cluster on the corrin template.

Carbon monoxide is known to form adducts with porphyrin [6] and with many inorganic compounds [4]. However, the high energy clusters are more stable when calculated at the MP2 level which requires more resources. Accordingly, the substituents here are all hydrogen atoms, as shown in the diagram, Fig. 2.

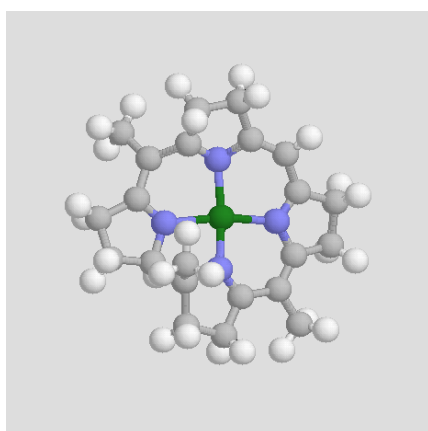
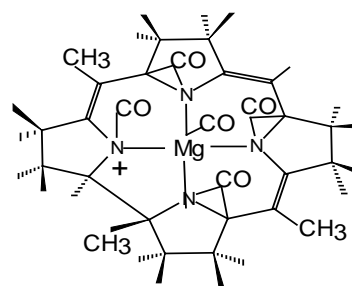
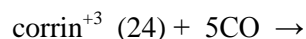


Fig.2. corrin<sup>+3</sup> (24) Abbreviated structure for Vitamin B12 template.

Here, it is assumed that five carbon monoxide molecules can bond in the form of aziridon-2-one cyclic rings [6], as shown,



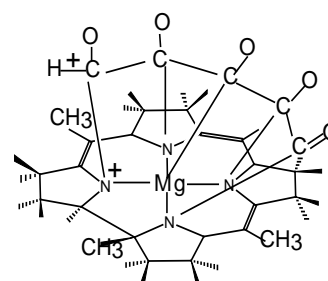
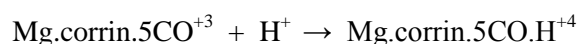
Mg.corrin.5CO<sup>+3</sup> adduct (25) [32]

$$\Delta H_{(\text{HF})} = 0.56934 \text{ h}$$

The enthalpy value suggests that several excitations would be necessary for all the carbon monoxide molecules to be promoted to this high energy state where a single excitation (0.21 h) is greater than the activation energy [6]

#### 3.7.2. The formation of the $\alpha$ -D-ribose backbone on the corrin template.

It is expected that when excited with UV radiation with an in-plane electron transition, the carbon monoxide adducts will experience a magnetic torque perpendicular to the surface of the corrin ring when viewed from above in accordance with Lenz's Law, enabling bonding and the binding of a proton, as shown, leading often to a D-sugar [10].



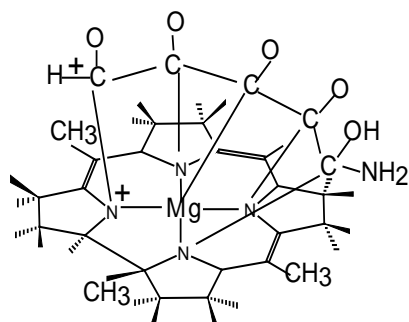
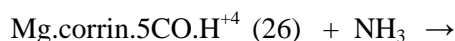
Mg.corrin.5CO.H<sup>+4</sup> (26) [33]

$$\Delta H_{(\text{HF})} = -0.33752 \text{ h}$$

The oxygen atoms all carry negative net Mulliken charges near -0.23, and are susceptible to protonation. The ketone group is available for reaction with a base such as 5,6-dimethyl benzimidazole. This is approximated here with a

reaction with ammonia to reduce the number of atoms and the computation time.

### 3.7.3. The formation of the $\alpha$ -D-ribose ammonia backbone on the corrin template.



$$\Delta H_{(\text{HF})} = -0.03157 \text{ h}$$

## 3.8 The formation of the phosphodiester bond between the corrin link and the $\alpha$ -D-ribose on the corrin template

### 3.8.1. The partial hydrogenation of the $\alpha$ -D-ribose ammonia backbone on the corrin template.

With the increase in the number of atoms and iteration time, these calculations are at the HF level with only the link substituent present on the corrin template. To correlate the previous calculations and the corrin now carrying the preformed  $\alpha$ -D-ribose, a further truncated corrin substituted molecule is used, designated as Mg.corrin(28) as shown in Fig.3.

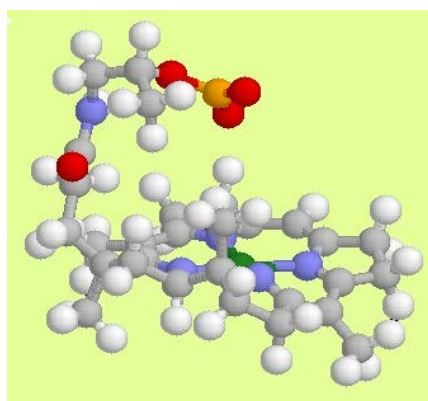
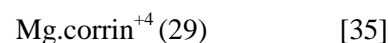
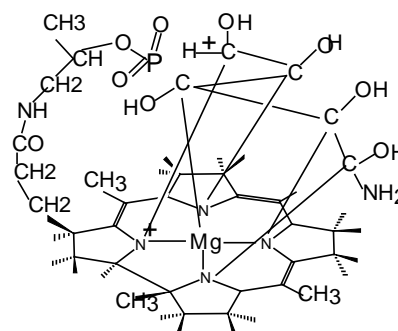
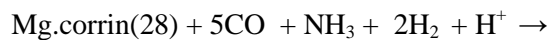


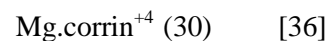
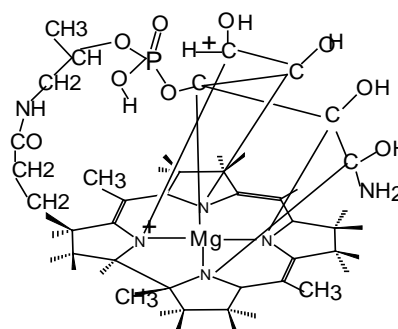
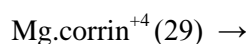
Fig.3.Mg. corrin(28)



$$\Delta H_{(\text{HF})} = 0.17972 \text{ h}$$

The molecule is expected to obtain electrons from the photolysis medium and easily change its oxidation state [22] by electron ejection or capture.

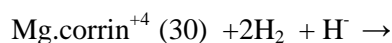
### 3.8.2. The formation of a phosphate linkage between the corrin metaphosphate and the $\alpha$ -D-ribose.

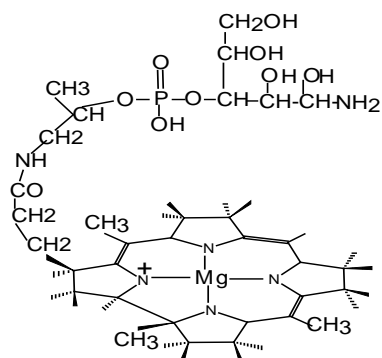


$$\Delta H_{(\text{HF})} = 0.01243 \text{ h}$$

This mild reaction [23] is expected to be augmented by the ionization of the orthophosphate di-ester.

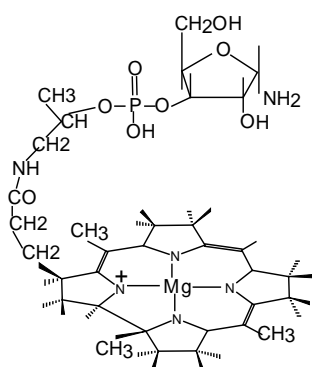
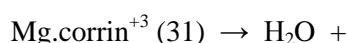
### 3.8.3. The further hydrogenation of the 3'- $\alpha$ -D-ribose ester.



Mg.corrin<sup>+3</sup> (31) [37]

$$\Delta H_{(\text{HF})} = -0.99572 \text{ h}$$

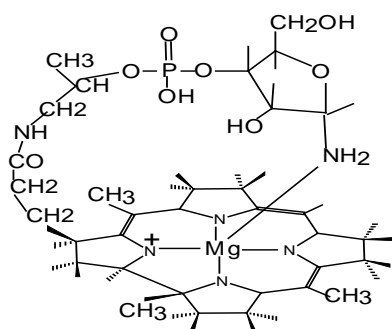
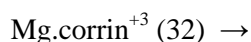
### 3.8.4. The closure of the $\alpha$ -D-ribose ammonia on the corrin template.

Mg.corrin<sup>+3</sup> (32) [38]

$$\Delta H_{(\text{HF})} = 0.02559 \text{ h}$$

### 3.8.5. The coordination of the $\alpha$ -amino D-ribose with the Mg.corrin.

The rotamers enable the coordination to occur with the metal ion in an energetically favourable reaction.

Mg.corrin<sup>+3</sup> (33) [39]

$$\Delta H_{(\text{HF})} = -0.08437 \text{ h}$$

## 4 Conclusion

These calculations suggest that this molecule may once have been prevalent on the surface of the Earth if the prebiotic atmosphere was mildly reducing and the environment slightly alkaline, but its synthesis would be challenging in the absence of the reactants depicted here. The complexes are stabilized by metal ions such as the cobalt ion and should be able to acquire a number of oxidation states.

Further work at a higher accuracy may alter the values given here.

## 5 Acknowledgements

Appreciation is expressed for the advice and support given to this project by Professor Curt Wentrup of the University of Queensland.

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